

Electron Concentration as a Guide to Alloying Behaviour

ENGEL-BREWER AND THE PLATINUM METALS

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Some unexpected reactions in platinum metal alloys have been successfully predicted by the Engel-Brewer relationships. Although the basic principles involved are still uncertain, interesting possibilities emerge and several possible applications for the reactions suggested by this theory are proposed.

The practical metallurgist is rarely able to make use of theoretical predictions and much of the interest aroused by the Engel-Brewer correlation stemmed from its claims of direct utility in the design of transition metal alloys. Although Hume-Rothery (1) has demonstrated the unsound foundations of some parts of the theory most of the failures he discussed were associated with the metallurgy of copper, silver and gold. In the transition element field considerable successes have been achieved and one is encouraged to consider the practical implications of these ideas and how these might lead to the development of new commercially viable materials.

Pure Metals

In his early attempts (2) to correlate the stable crystal structure of metals with the electron configuration of free atoms Engel predicted that bond strength was determined almost completely by the number of d electrons participating. This conclusion has since been qualified by Brewer (3, 4) who now suggests that over the main range of the transition elements the bonding energy of the s and p electrons is greater than that of the d electrons. The type of crystal structure adopted is still, however, regarded as being determined by the s and p electrons alone, the b.c.c., c.p.h., and f.c.c. structures cor-

relating to 1, 2 and 3 ($s+p$) electrons per atom.

Over the three transition series the bonding effectiveness of a d electron falls to a minimum when the number of unpaired d electrons arrives at a maximum of 5 per atom. The magnitude of the d bond strength increases with progress from the first to the third long period.

The stability of the crystal structures as predicted from Brewer's calculations is determined by the difference between the total bonding energy and the original promotional energy assumed. Tungsten offers a good illustration of the methods of calculation adopted. The ground state of tungsten is $d^4 s^2$, and the two s electrons would appear to indicate a close-packed hexagonal crystal structure. The promotional energy associated with the change from the $d^5 s$ configuration is only 8 kcal/mole, however. Since this slight expenditure of energy releases six electrons for bonding the most stable structure, associated with the single s electron is of course b.c.c.

Such arguments are used to explain the change from b.c.c. to c.p.h. structure on passing from tungsten and molybdenum to elements of higher atomic number. If the additional electrons entered the d orbital, pairing would occur, the number of electrons

available for bonding would decrease, and the stability of the structure would fall catastrophically. Such a fall is avoided by a change in electron configuration. Thus, if the configuration $d^6 s$ is changed to $d^5 sp$, all five d -orbitals are made available for bonding and the close-packed hexagonal structure is thereby stabilised. In the neighbourhood of tungsten the promotional energies associated with such changes in configuration are claimed to be negligible compared to the improved bonding energies obtained. Movements to the right of osmium and ruthenium involve a change from the $d^{n+5} sp$ configuration to that of $d^n s p^2$, which by placing three electrons outside the d shell makes more electrons available for bonding and stabilises the f.c.c. structure.

Increasing refinement in Brewer's treatment has shown that such integral configurations can only be approximate, and the optimum configurations required for the most stable structures are non-integral. Thus the optimum configuration for ruthenium is $d^{6.3} s p^{0.7}$ rather than the $d^6 s p$ configuration originally proposed.

The promotional energies involved in such configuration changes increase as the right-hand side of the three transition series are approached and this increase is used to explain the decrease in melting-point and increase in vapour pressure with increasing atomic weight. The assumption that melting-points and vapour pressures provide a true index of crystalline stability is, of course, very dubious, and the errors involved in an attempt to predict the melting-point of gallium from its vapour pressure would be considerable.

Osmium and iridium have the highest elastic moduli of any of the metals. They also have the lowest compressibilities and it does not seem likely therefore that bonding processes deteriorate rapidly as soon as tungsten is left behind.

The main weakness of the configurational adjustments referred to above has been well exposed by Hume-Rothery (1). Thus the

simple electronic concentrations are translated into configurations which satisfy the Engel correlation. Conclusions based on these translated values could in most instances have been reached on the basis of simple electronic concentrations alone. Such correlations were considered by Robins (5) who in 1959 suggested that a tendency exists for the number of bonding electrons per atom to equal half the co-ordination number. This tendency explains why tungsten and molybdenum, each presumed to have six valency electrons and an effective co-ordination number of 12 have the highest melting-points in their respective series. The change in crystal structure on passing from tungsten to rhenium helps to maintain this two-to-one ratio and thus stabilises the hexagonal structure.

Alloys

In the prediction of alloy-phase equilibrium Brewer (4) made considerable deviations from the integral electron concentration values used for pure metals. In the copper, silver and gold alloys the treatment was largely unsuccessful and it has not been explained, for example, why the composition ranges of α and β brass overlap.

The treatment of transition metal alloys has been rather more successful. The $(s+p)$ electron concentration ranges associated with the b.c.c., c.p.h., f.c.c. phases are respectively 1.0-1.5, 1.7-2.12 and 2.5-3. Taking the basic electron configuration of molybdenum and tungsten as $(4d^5)(5s)^1$ Hume-Rothery (1) has used these concentration ranges to calculate the solubility limits shown in the table in these two metals.

Reasonable agreement has been obtained particularly when the solvent and solute are close together in the Periodic Table. The effect of temperature upon solubility does not clearly emerge from the various publications involved. This is obviously of great importance, and Selman (6) has recently shown that the solubility of platinum in molybdenum increases from approximately 2 atomic per

Solubility Limits predicted by the Engel-Brewer Correlation					
Solvent	Solute		Solubility Limits in Atomic Per Cent		
			Predicted by Brewer	Experimental	
Molybdenum	Tc	Re	50	50	43
	Ru	Os	25	30.5	17
	Rh	Ir	17	20	16
	Pd	Pt	12.5	6	> 10
Tungsten	Re	Tc	50	37	?
	Os	Ru	25	18.5	23
	Ir	Rh	17		
	Pt	Pd	12.5	4-6	5

cent at 1400°C to more than 10 atomic per cent at 1700°C. Although Brewer states that "the Engel correlations make thermodynamic predictions and must therefore be valid for the entire temperature range" (7), it would be interesting to see a practical application of this philosophy to the calculation of a temperature solubility curve.

Stable Platinum Metal Compounds

An important feature of the Engel-Brewer theory is the prediction that metals from opposite ends of the second and third transition series should react strongly with each other to form compounds of high stability. This subject has been briefly referred to in a previous article (8).

By reacting platinum with stable carbides Brewer (8) formed an estimate of the free energies of formation of these compounds. Thus, platinum reacted with zirconium carbide to produce the hexagonal compound $ZrPt_3$. Since zirconium carbide has a free energy of formation of -47 kcal/mole, the free energy of formation of $ZrPt_3$ was presumed to be higher. It is difficult, however, to pursue such arguments to their logical conclusion. It is known that all the carbides can be dissociated by heating in contact with the platinum metals and in no instance does the formation of a compound appear to be

necessary. If an excess of platinum is employed the end product is a dilute solution of the transition element in platinum, and the main function of the platinum is to keep the activity of the carbide-forming element at a low level. Molybdenum and tungsten carbide are readily dissociated in this way although there should, according to the Brewer-Engel correlation be no driving force for this reaction. Molybdenum carbide is by no means as stable as zirconium carbide. Both these compounds are, however, far less stable than alumina, which has been shown (9) to be readily dissociated under unoxidising conditions in the presence of platinum, which takes the aluminium into solid solution at temperatures above 1400°C.

Accurate thermodynamic measurements on zirconium-platinum alloys are obviously required. The electron negativities of the two metals are very different and a fairly high heat of reaction would be suggested by this fact alone (1). The transference of charge in such a reaction would, however, be in the opposite direction to that proposed by Brewer.

Some Practical Applications

Whatever the mechanism of the reactions involved it seems that practical attention might well be devoted to the varied lines of thought suggested by the theory. Exothermic

fuses are one possibility. Here the hafnium wire would be sheathed with an appropriate thickness of palladium. Such a fuse wire would withstand corrosive conditions for long periods without failure, but would, if overheated disrupt explosively and provide instantaneous protection for the circuit.

Applications might also exist in the field of age-hardening and dispersion-strengthened alloys. Thus small quantities of yttrium and palladium, dissolved stoichiometrically in an inert metal matrix should react upon suitable heat treatment to produce a finely divided compound of considerable strengthening power (10).

Interesting possibilities can be discerned in the sintered carbide field. Cobalt, the normal cement used for the liquid-phase bonding of carbides is unfortunately not very resistant to oxidation at high temperatures and this restricts the high temperature applications of such materials. Palladium or a palladium-based alloy would be more resistant to oxidation and would also react chemically with the carbide in the way

described by Brewer. By suitably proportioning the amount of palladium added to the carbide mixture improved oxidation resistance might be achieved with stronger chemical bonding between the cement and the carbide. Appreciable improvements might result even if the palladium replaced only a small proportion of the cobalt binder (11).

References

- 1 W. Hume-Rothery, *Progress in Materials Science*, 1967, 13, (5)
- 2 N. Engel, *Kem. Maanesblad*, 1949, Nos 5, 6, 8, 9, 10
- 3 L. Brewer, Prediction of High Temperature Metallic Phase Diagrams, U.C.R.L. - 10701, UC-25 Metals, Ceramics and Materials, 1963
- 4 L. Brewer, *High Strength Materials*, Ed. V. F. Zackay, New York, John Wiley, 1965
- 5 D. A. Robins, *J. Less-Common Metals*, 1959, 1, 396
- 6 G. L. Selman, *Platinum Metals Rev.*, 1967, 11, 132
- 7 L. Brewer, *Acta Metall.*, 1967, 15, 553
- 8 A. S. Darling, *Platinum Metals Rev.*, 1967, 11, 138
- 9 A. S. Darling, *Metals Mater.* 1968, 2, (1), 28
- 10 Johnson Matthey, Provisional Patent Appl. 29958/67, 3520/68
- 11 *Ibid.*, 12720/69

A Rhodium-Platinum Probe for Flame Velocity Measurement

A probe for velocity vector measurements in flames consists of a spherical tip with one pressure point on the axis and four others spaced equally around it at 40° to the central point. Pressure differences between opposite pairs of these holes, when referred to the pressure at the central point, give gas flow direction and velocity. Stainless steel probes are suitable for cooled airflows or, when water-cooled, for large industrial furnaces, but in the relatively much smaller dimensions of gas turbine combustion systems the application of this technique depends on devising a method permitting the construction of compact probes in a manner suitable for use at kerosene-air flame temperatures.

A technique of construction has recently been developed at the National Gas Turbine Establishment in which both the spherical probe head and the five lengths of hypodermic tubing are fabricated in 20 per cent rhodium-platinum, the whole then being brazed to

a stainless steel water-cooled probe body. The stainless steel hypodermic extension tubes and water jacket then pass through a cylindrical brass block, carrying a 360° scale to indicate angle of rotation, to a cluster of unions. This assembly can be used in flame temperatures up to 1800°C.

A complete water-cooled probe unit in which the rhodium-platinum head is nickel-brazed to the stainless steel probe body

